Monitoring & Assessment of Toxics in Delaware Surface Waters

Rick Greene

Watershed Assessment Branch

April 5, 2013

Outline

- Background
- Partners
- Past, present, and future projects
- Emerging contaminants
- Opportunities to collaborate

Background on DNREC

- State agency responsible for protecting/managing Delaware's natural resources. Established 1970.
- Currently, 7 major Divisions organized around specific media (air, water, land) or functions.
- 2012 budget ~ $81.9M (43.2% State GF & 56.8% Fed). FTEs – 794 (721 filled).
- No stand-alone, overarching research program. Applied research, if any, is embedded in individual programs.
- Watershed Assessment Branch within the Division of Watershed Stewardship provides science-based assessments used to help inform management decisions.

Context

- Delaware: Small State with diverse land uses; urban/industr to the north, rural/agric to the south
  - *Former "Chemical Capital of the World"*
  - *We border the Del Estuary, which hosts largest freshwater petro port on East Coast*
  - *Delaware is downstream from Philly/Camden.*
  - *Wilmington was significant player in shipbuilding & tannery business*
- Many current & past sources of toxics:
  - *Petroleum refining, pesticide manufacturing, acids/bases, pigments, paper, steel, metal plating, cleaning solvents, batteries, electrical generation & delivery, transportation, pharma, turf management, agriculture (pesticides, herbicides, & pharma), and other specialty products*
- "Delivery System" to surface water:
  - *Point sources: WWTPs, stacks, waste sites, muni landfills, storage tanks*
  - *Nonpoint sources: stormwater runoff, groundwater discharge, atmospheric deposition*
- Monitoring has identified many types of toxic chemicals in Delaware's water, sediment & biota:
  - *PCBs, OC pesticides, PAHs, metals, PBDEs, pharma & personal care products*

Monitoring Objectives

- Status & trends in surface water, sediments & biota
- Fate processes (*e.g., chemical partitioning & speciation, which influence bioavailability & toxicity*)
- Assess/quantify significance of release from sources to surface waters
- Assessing risks to aquatic life, wildlife, & humans
- Technical support for regulatory decisions (*e.g., 303(d) listings & TMDLs, NPDES limits, waste cleanup plans, NRDA associated with spills & past releases*)
- Test new field & laboratory methods (*e.g. in-situ high volume sampling, SPMDs, black carbon, HRGC/HRMS, C&N isotopes for foodchain*)

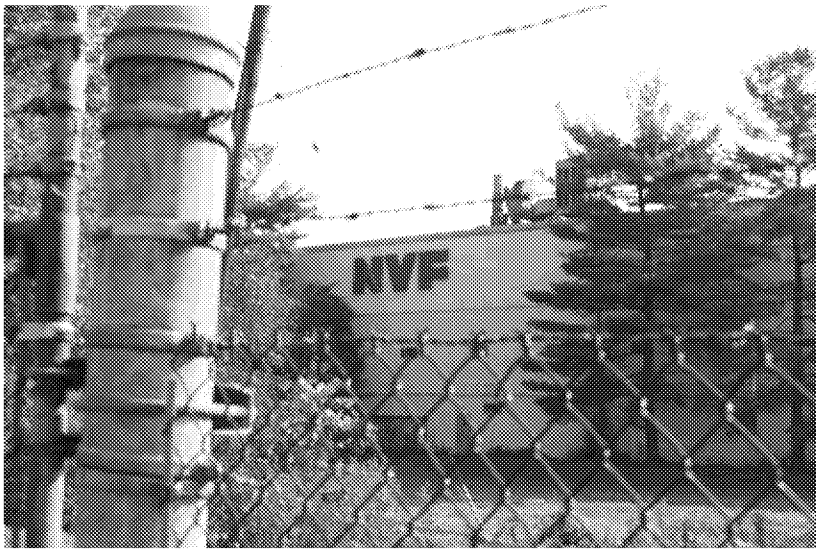
Partners (partial list)

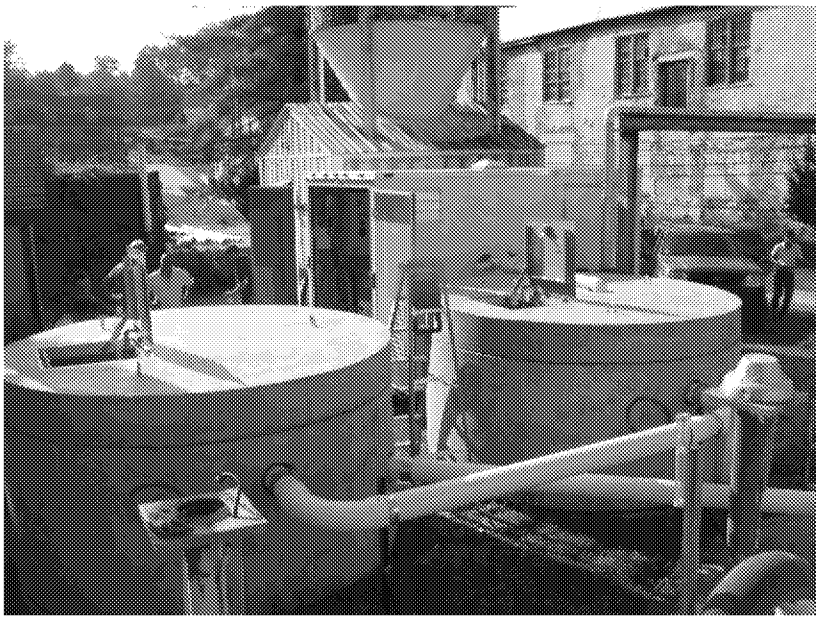
- State agencies (DNREC, DHSS, DA, DelDOT), County and Municipal governments
- Federal agencies (EPA, NOAA, USFWS, COE, USGS)
- DRBC, Basin States, & PDE
- UD (DGS, Earth & Ocean, Ag, Engineering, Sea Grant)
- Academy of Natural Sciences of Philadelphia (ANSP)
- Other Academics: UConn, Dartmouth, UMBC
- Private Labs (e.g., AXYS, TestAmerica) & Consultants

Selected Past Projects

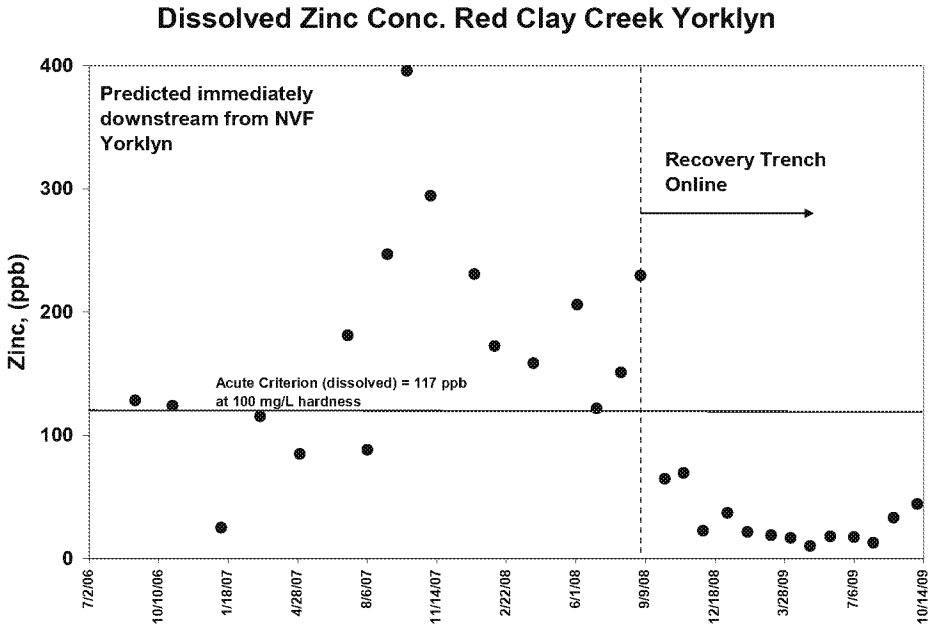
- ***Red Clay Creek Zinc TMDL***
- ***Christina Basin sediment core dating & pollution histories***
- ***Arsenic in the Inland Bays***
- Monitoring toxicity in the Delaware Estuary
- M/V Athos I Oil Spill
- Red Clay Creek contaminant uptake in stocked trout
- Delaware Estuary fish tissue database

Red Clay Creek Zinc TMDL

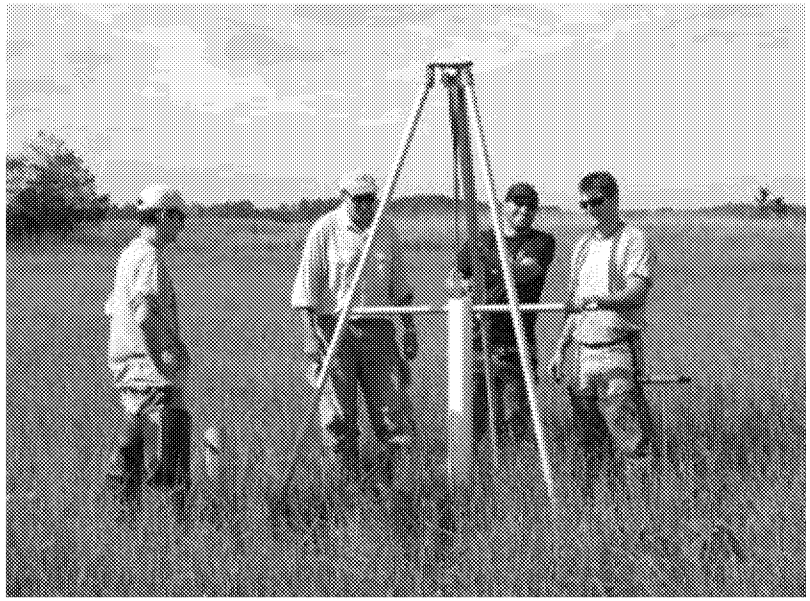




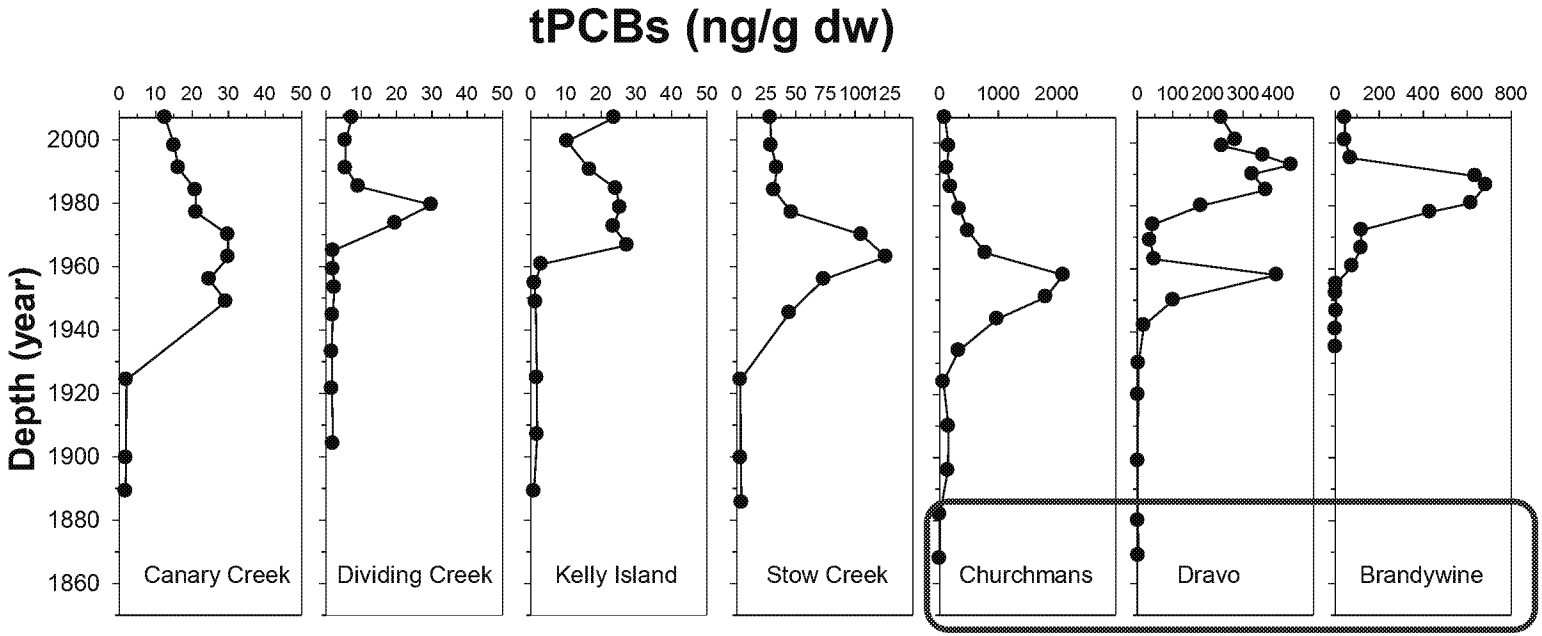
- NVF Yorklyn manufactured vulcanized fiber from 1900 to ~2005. Zinc used in process.
- Recycle line crushed, releasing copious supply of dissolved zinc to groundwater, which then discharges to Red Clay Creek.
- Zinc TMDL adopted, appealed & revised based on lognormal probability analysis
- Zinc recovery system installed Fall 2008
- Site being repurposed



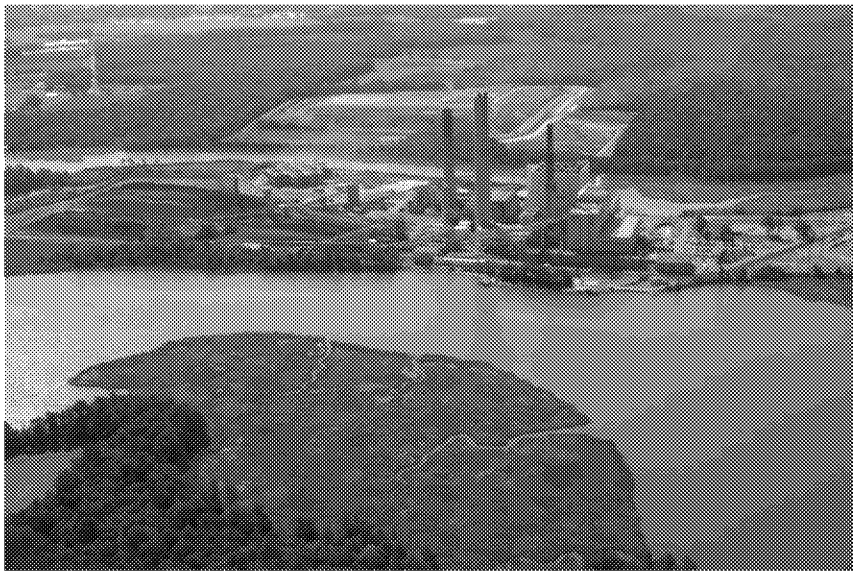
Sediment Dating & Pollutant Histories



- ANSP/UDEL collected 3 sediment cores from tidal Christina Basin 2007/2008
- Cs-137 & Pb-210 isotopes provide geochronology & sedimentation rate
- Analysis of core slices for PCBs & other COCs provide pollution histories.
- Cores from the tidal Christina Basin part of larger effort to understand PCB trends & fate in DE Estuary.



Arsenic in the Inland Bays



FATE AND TRANSPORT OF ARSENIC IN DELAWARE SOILS:
ASSESSING POTENTIAL IMPACTS ON WATER QUALITY

Final Report

SUBMITTED BY:

Dr. D. L. Sparks
Dr. J. Thomas Sims
Jennifer Seiter
Sheila Gardner
Department of Plant and Soil Sciences
College of Agriculture and Natural Resources
University of Delaware
Newark, DE 19717-1303

SUBMITTED TO:

Richard Greene
DNREC, DWR, Watershed Assessment Branch
820 Silver Lake Blvd., Suite 220
Dover, DE 19904-2464
Ph: (302) 739-4590

FEBRUARY 23, 2007

UNIVERSITY OF DELAWARE

- Inland Bays located southeastern Sussex Co.
- IRPP near Millsboro. Public concern over coal ash pile.
- Data compiled & assessed. Findings:
  - ✓ No widespread problem
  - ✓ Fish/shellfish safe to eat
  - ✓ Arsenic at IRPP is localized
  - ✓ Drinking water doesn't exceed MCL
  - ✓ Use of Roxarsone not sustainable

Arsenic in Inland Bays Fish/Shellfish

Integrated Environmental Assessment and Management — Volume 3, Number 4 — pp. 544–554
© 2006 SETAC

Total and Inorganic Arsenic in Mid-Atlantic Marine Fish and Shellfish and Implications for Fish Advisories

Richard Greene*† and Eric Cecalaist

†Delaware Department of Natural Resources and Environmental Control, 820 Silver Lake Boulevard, Suite 220, Dover, Delaware 19904-2464, USA
‡Battelle Marine Sciences Laboratory, 1529 West Sequim Bay Road, Sequim, Washington 98382, USA

(Received 23 April 2007; Accepted 6 February 2006)

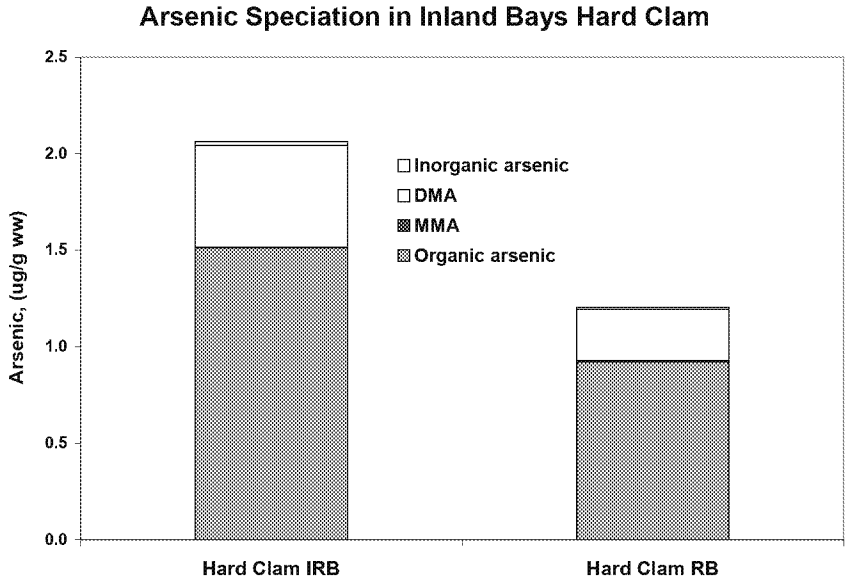
ABSTRACT

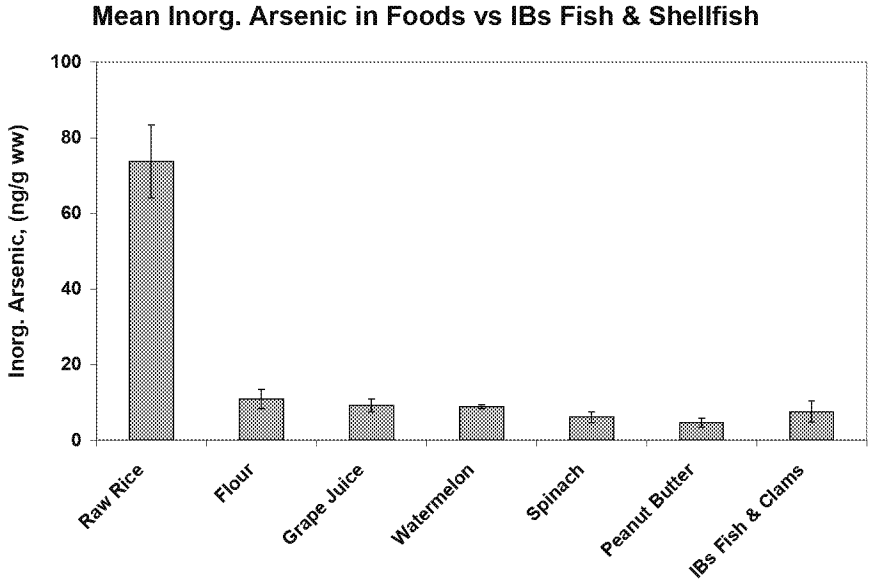
Sampling was conducted in 2002 to determine the total concentration and chemical speciation of arsenic in several marine fish and shellfish species collected from the Delaware Inland Bays and the Delaware Estuary, both of which are important estuarine waterbodies in the US Mid-Atlantic region that support recreational and commercial fishing. Edible meats from summer flounder (*Paralichthys dentatus*), striped bass (*Morone saxatilis*), Atlantic croaker (*Micropogonias undulatus*), and hard clam (*Mercenaria mercenaria*) were tested. Total arsenic was highest in summer flounder, followed by hard clam, then striped bass, and finally Atlantic croaker. Total arsenic was higher in summer flounder collected during the spring, as these fish migrated into the Inland Bays from the continental shelf, compared with levels in summer flounder collected during the fall, after these fish had spent the summer in the Inland Bays. Similarly, striped bass collected in the early spring close to the ocean had higher total arsenic levels compared with levels detected in striped bass collected later during the year in waters with lower salinity. Speciation of arsenic revealed low concentrations (0.00548–0.02 ug/g ww) of all of toxic, inorganic arsenic. Dimethylarsinic acid was more than an order of magnitude greater in hard clam meats than in the other species tested, a finding that was attributed to arsenic uptake by phytoplankton and subsequent dietary uptake by the clam. Risk assessment using the inorganic arsenic concentrations was used to conclude that a fish consumption advisory is not warranted.

Keywords: Arsenic speciation · Fish tissue · Fish advisories

Original Article

- Detailed study of total arsenic & arsenic speciation in biota performed 2002
- [As] greater in incoming flounder than outgoing flounder
- Inorganic (toxic) arsenic is small % of total arsenic (ave. = 1.2%)
- [As] in IBs fish/shellfish no different than other common foods.
- Risk assessment: No advisory needed

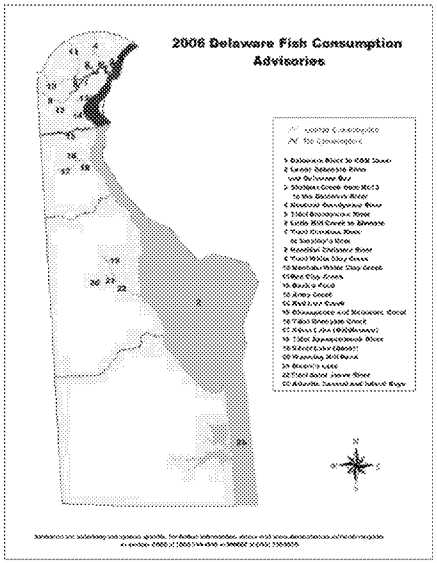




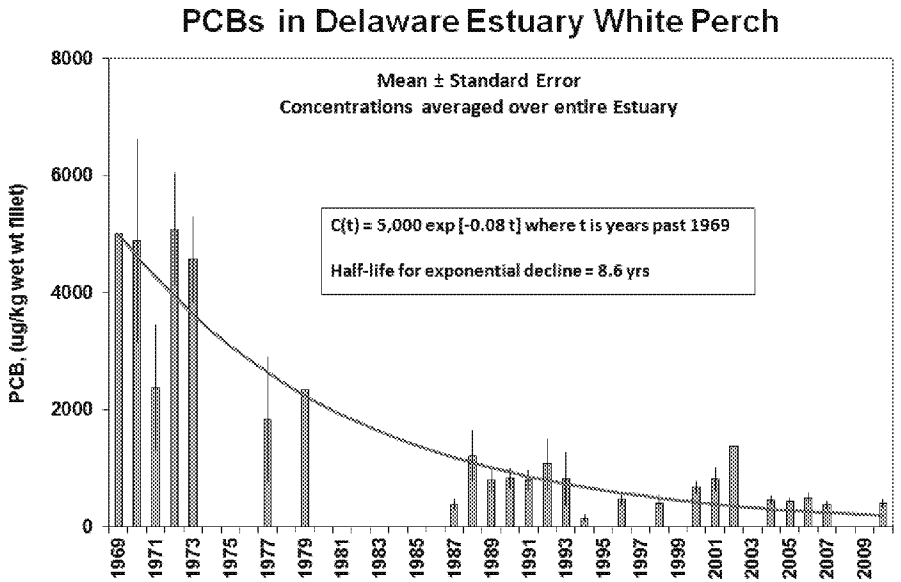
Current & Ongoing Projects

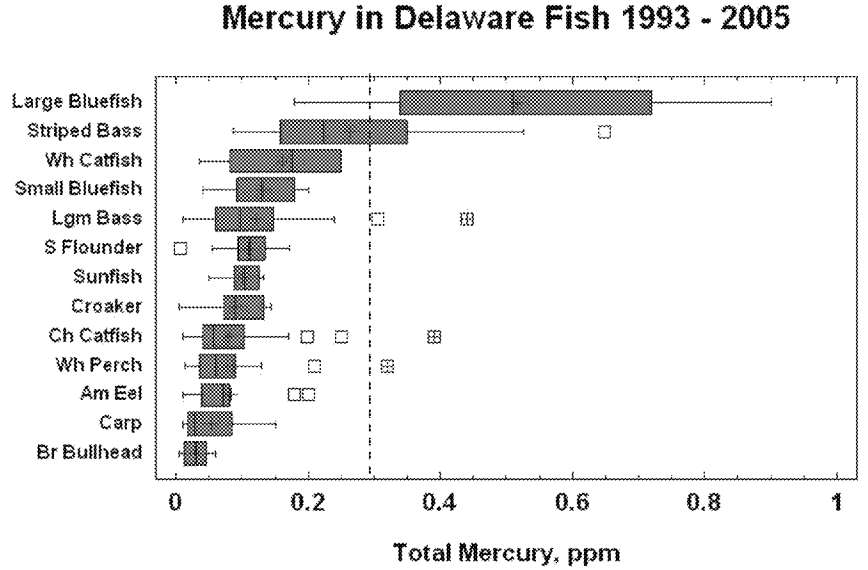
- ***Toxics in Biota Monitoring & Advisory Program***
- ***City of Wilm/NCC PCB Sewershed Trackback***
- ***Delaware River Main Channel Deepening***
- ***PAH Pilot Study of semipermeable membrane devices in Delaware Estuary sediment & water column***
- Delaware Estuary PCB TMDL
- Partitioning of PCBs to POC, DOC & Black Carbon
- Cycling of Mercury in Zone 5 of the Delaware Estuary
- Meco Ditch/Little Mill Creek Project
- White Clay Creek Benthic Stressor Assessment

Toxics in Biota Monitoring

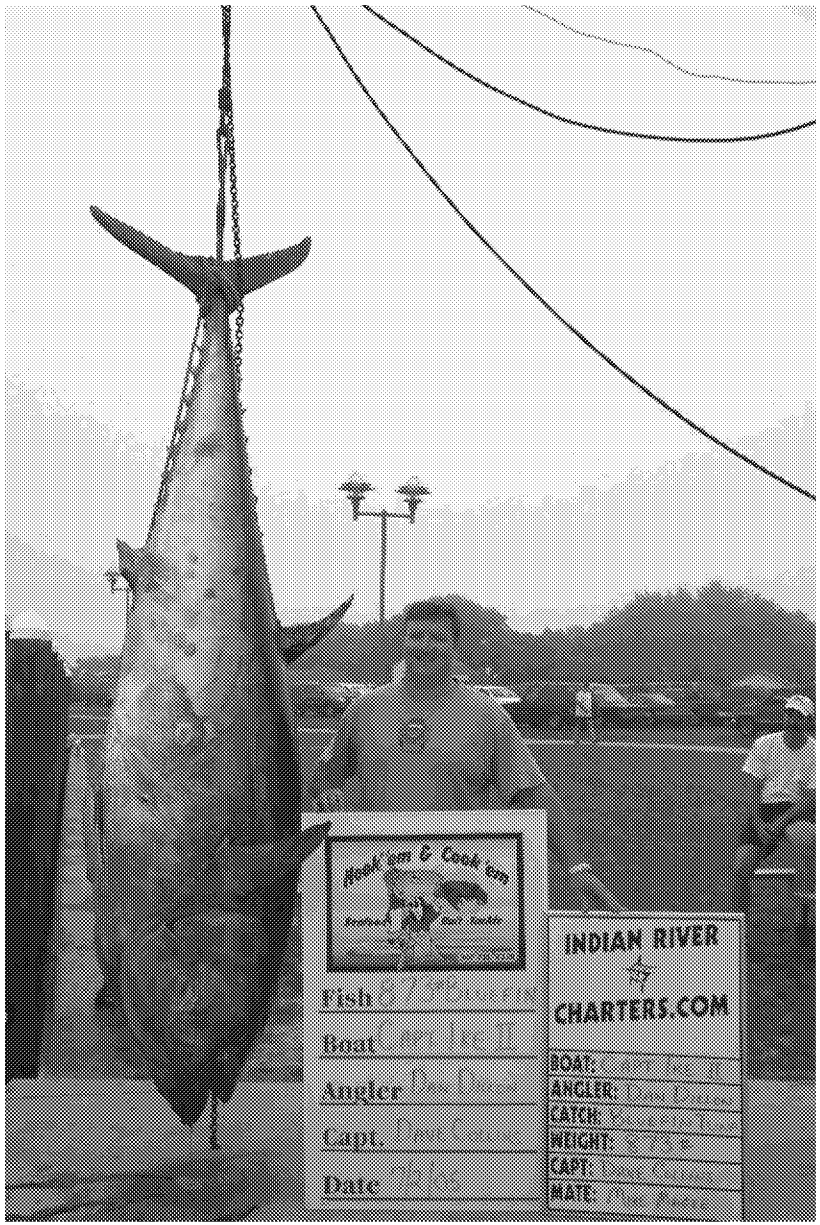


- DNREC has been testing fish/shellfish using advanced methods for ~25 yrs
- Data used to assess trends & to issue consumption advisories
- PCBs & DxF falling exponentially
- Large top predators most contaminated
- North to south gradient





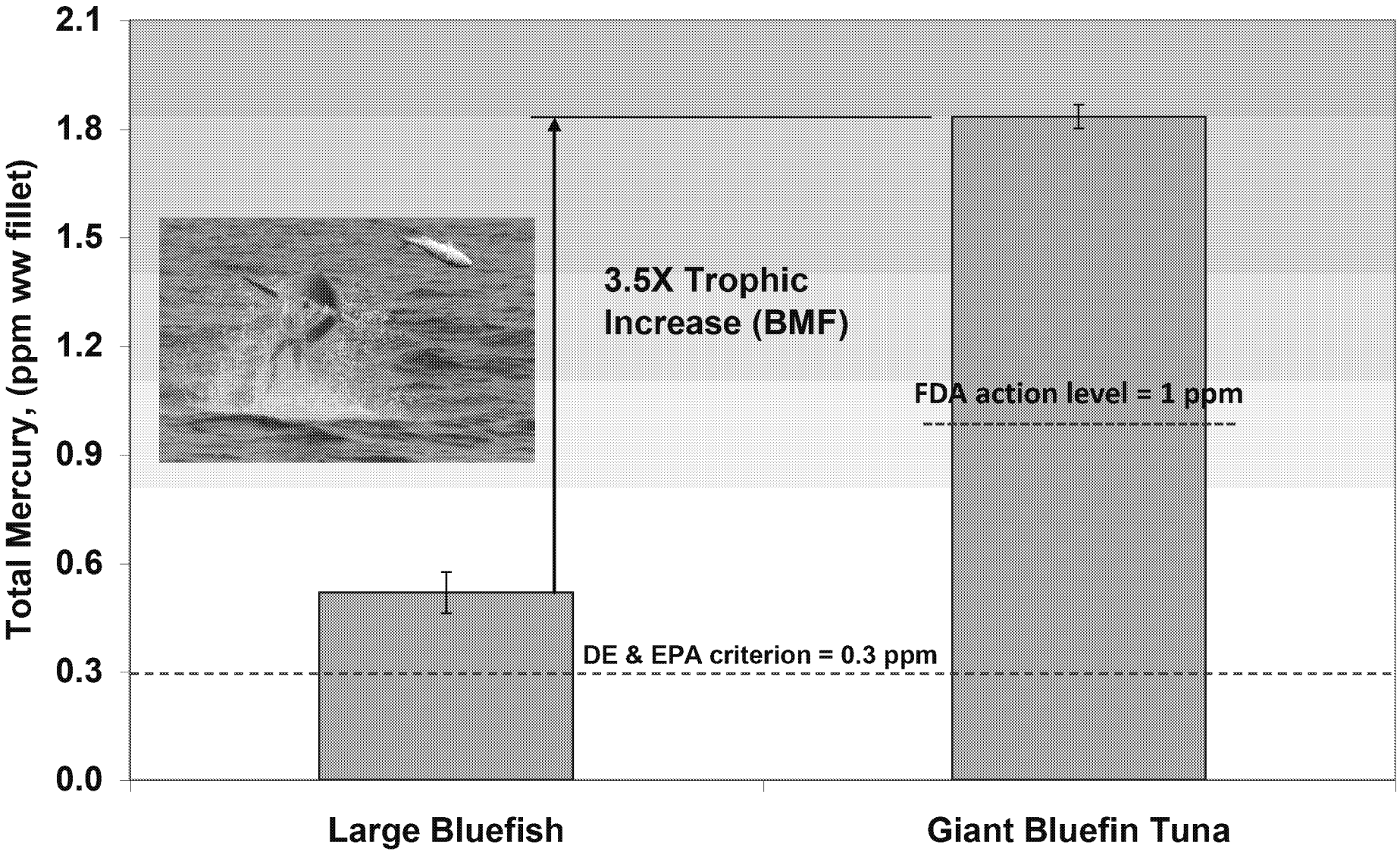
The Big Tuna



- Species: Bluefin Tuna
- 873 pounds; 9’ 6” long; 6’ 6” girth (State record)
- Caught July 2, 2005; Hot Dog Canyon (~40 miles E of IR Inlet)
- Age from charts: 30 yrs +/- 10 yrs.

So, how much mercury was in this apex predator?

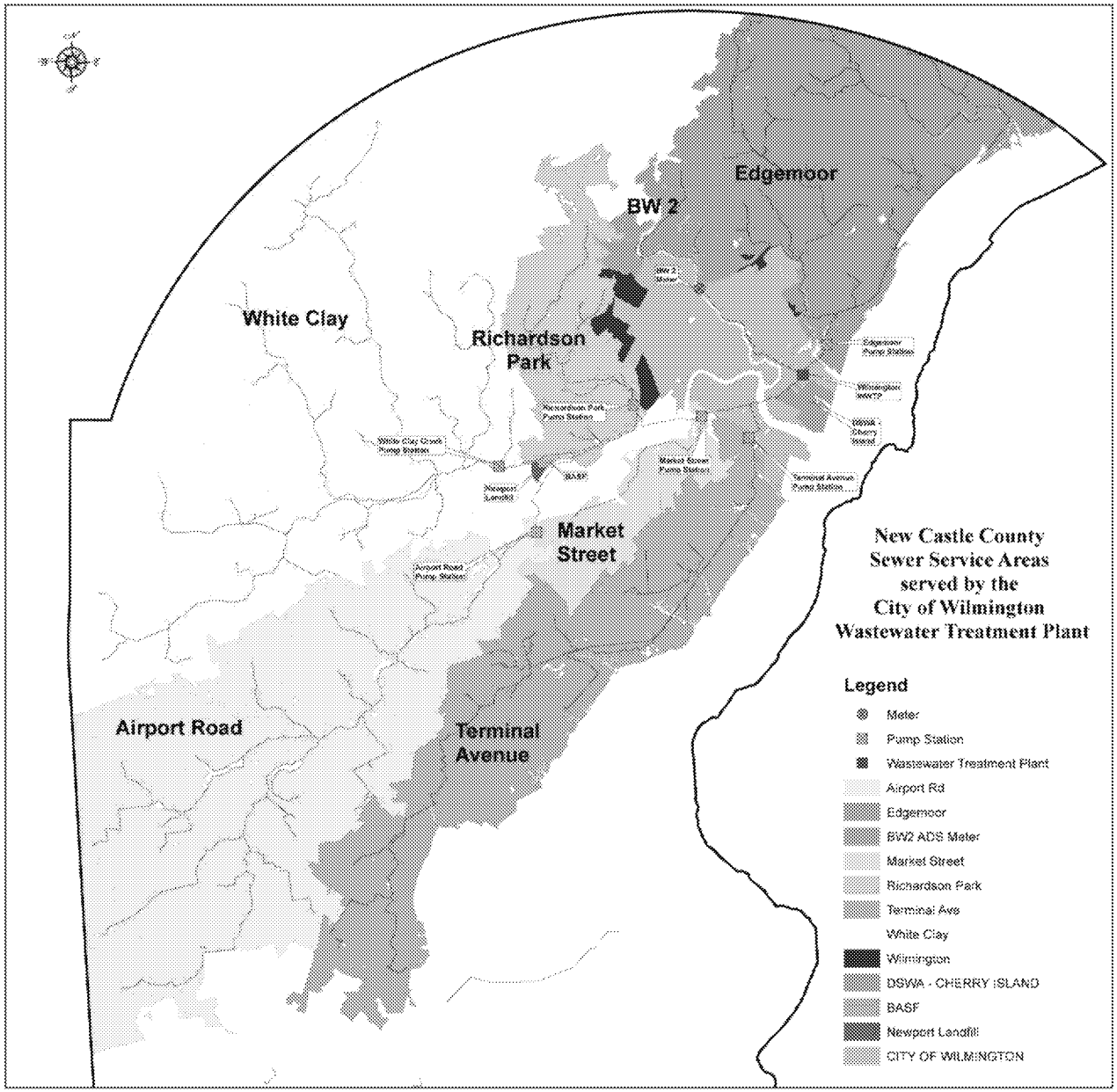
Trophic Increase of Mercury in Coastal Foodchain



PCB Sewershed Trackback

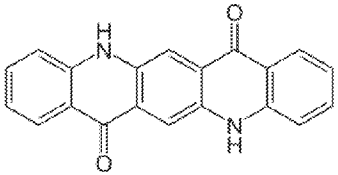
- City of Wilm has an NPDES permit to discharge treated wastewater to the Delaware Estuary.
- PCB discharge from the City's WWTP exceeds wasteload allocation established by EPA as part of the Total Maximum Daily Load (TMDL) for PCBs in the Delaware Estuary.
- The City's NPDES permit contains a special condition to reduce PCB mass loading to Estuary through a Pollutant Minimization Plan (PMP).
- Key element of the PMP is a PCB "trackback" study to identify PCB sources contributing to WWTP.

NCC & Wilmington Sewershed Map

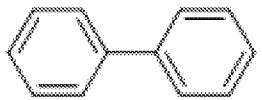


Inadvertent PCB Production

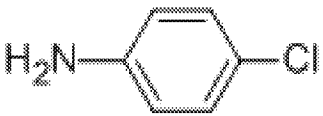
- Quinacridone pigment (QA) manufactured in Newport, DE.



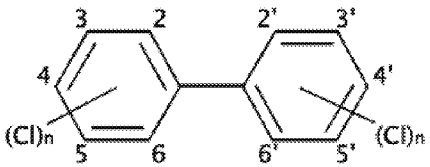
- Therminol VP-1 is used in QA synthesis. It contains ~26.5% Biphenyl, the basic building block of PCBs.



- Manufacturing process also involves chlorinated anilines (*used as a diazo component*).

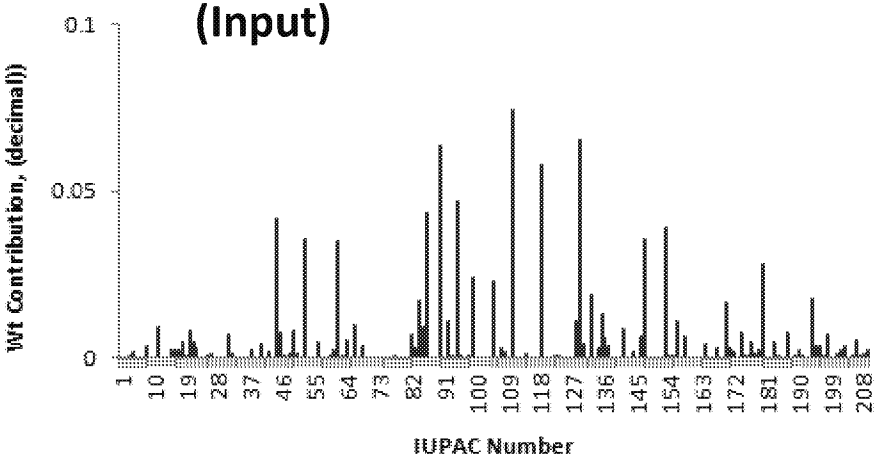


- Side-reaction of chloroanilines in the presence of biphenyl produces PCBs through a free radical mechanism.

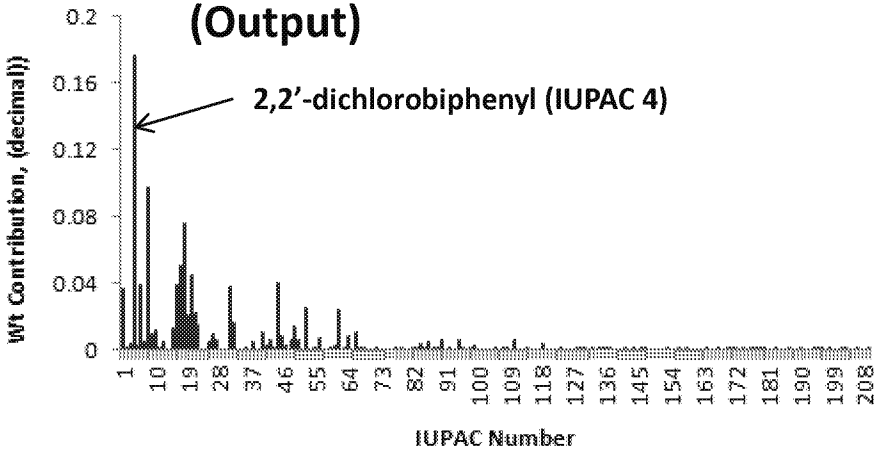


Partitioning & Dechlorination of PCBs in Regional Landfill

Typical Aroclor 1254 Fingerprint (Input)



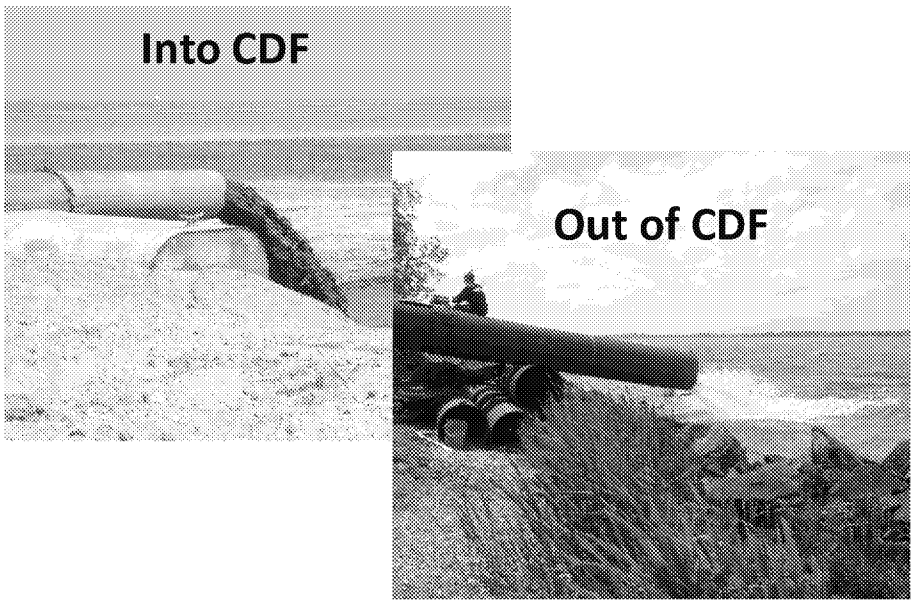
Typical Leachate Fingerprint (Output)

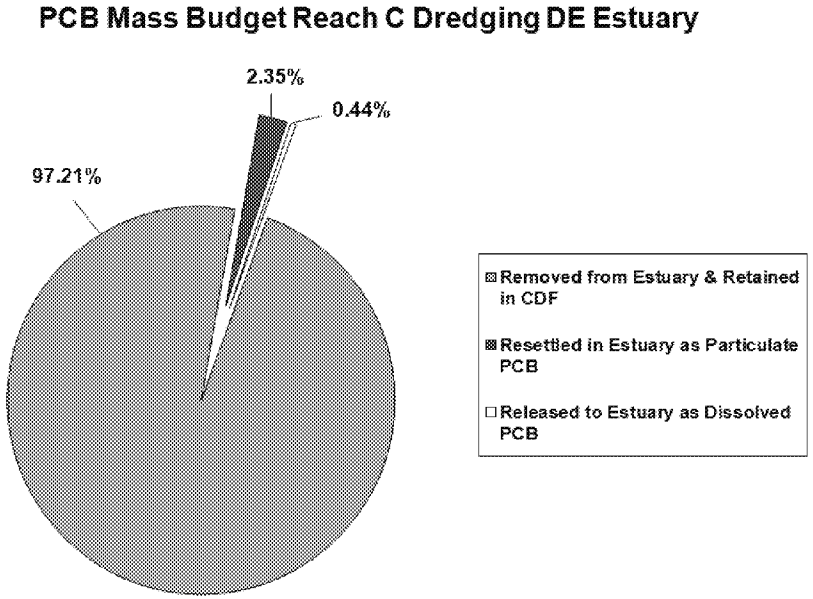


- Congener pattern of PCB input bears no resemblance to that of the leachate. Why?
- Landfills are rich in OC which acts as a sorbent. Landfills also act as large bioreactors where microorganisms help break down organic compounds.
- PCB **sorption** increases with chlorination. Heavier PCBs retained in the landfill and lighter PCBs released in the leachate.
- Further, **reductive dechlorination** selectively eliminates meta & para substituted congeners, leaving ortho PCBs. IUPAC 4 is ortho substituted & resists further decay.

Delaware River Channel Deepening

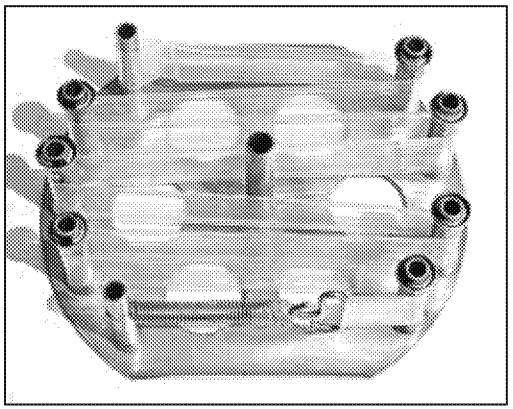
- Congress authorized deepening of nav channel from -40’ to -45’.
- DNREC worked with the COE to collect data behind the cutterhead, plus load into & out of the CDF.
- Mass balances show massive removal and few criteria exceedances.

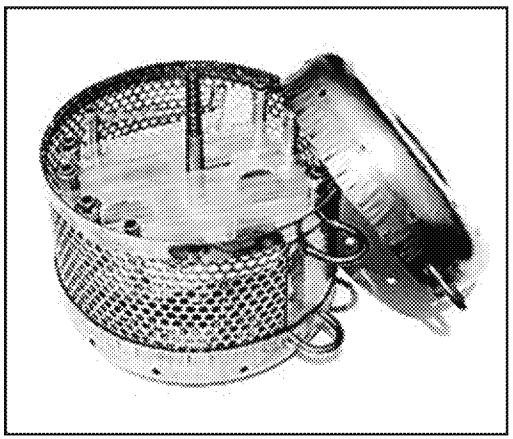




SPMD PAH Pilot Study

Semi-Permeable Membrane Device



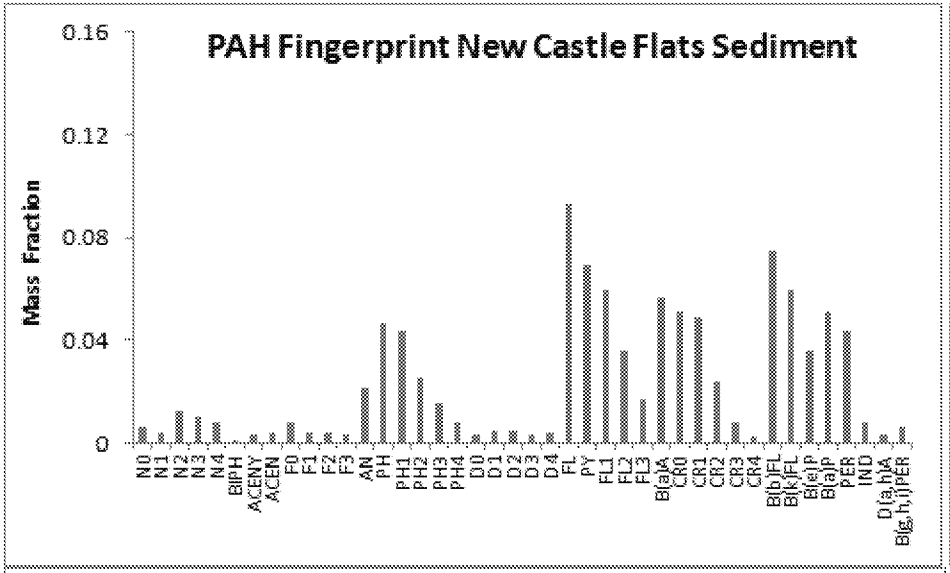


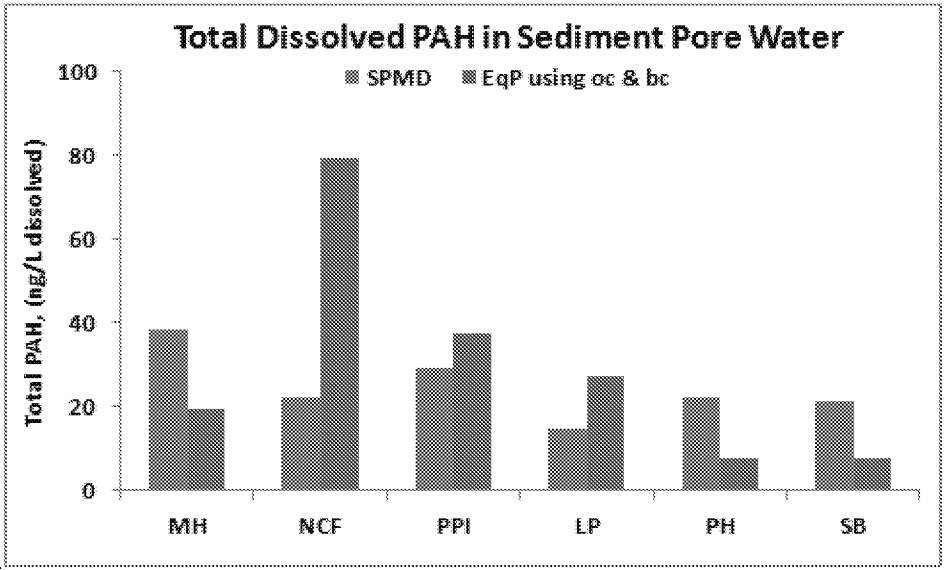
- SPMDs: flat tubing filled with lipid gel placed in stainless canisters.
- Deployed for 1 month in Del Estuary sediments, 2012.
- Dissolved phase PAHs in pore water partition into the gel (but don't get metabolized like in fish).
- Parent & alkylated PAHs extracted from gel and translated back to longer-term average dissolved conc.
- First time used in Delaware

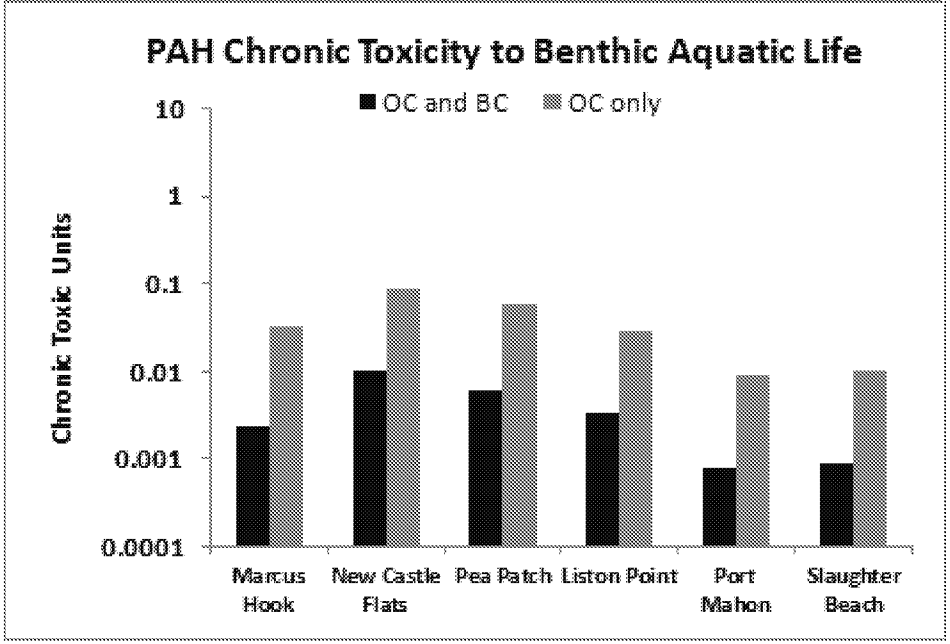
Selected a range of stations from high to low PAH concentrations in sediments

- Sediment grab samples were also collected half-way through the SPMD deployments.
- The grabs were collected adjacent to the SPMDs & were analyzed for the same parent & alkyl PAHs.
- Sediment grabs also analyzed for TOC & Black Carbon (BC) to permit EqP & narcosis calcs.

SPMD PAH Pilot Study Results







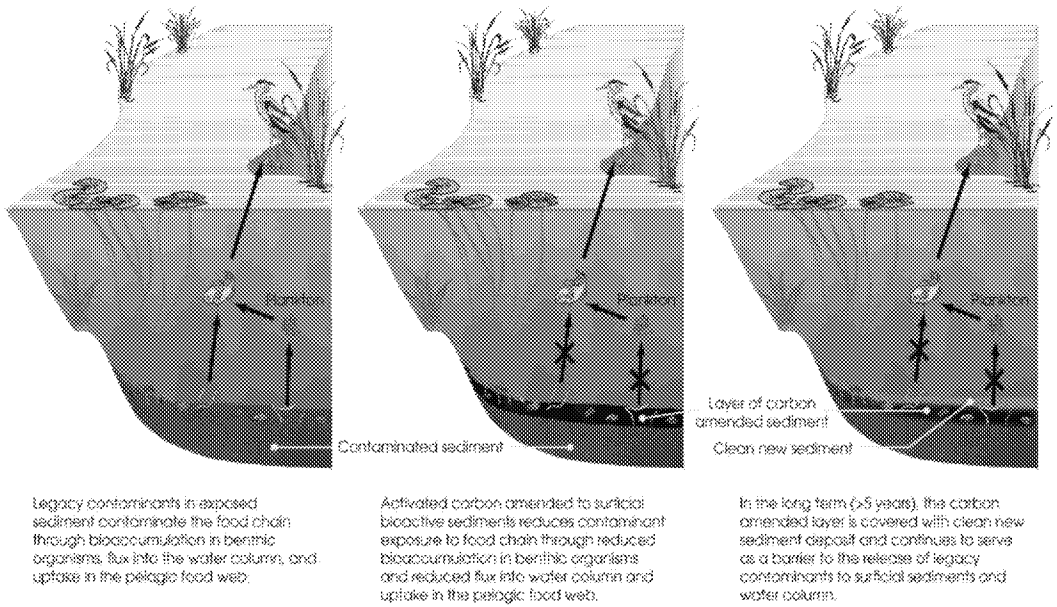
- Fingerprints highly similar across all stations (r = 0.89 to 0.99).
- Mostly HMW (pyrogenic) although widespread petrogenic PAH also present.
- Reasonable agreement between SPMD & EqP for dissolved PAH, PROVIDED black carbon considered.
- Narcotic toxicity not expected. Black carbon reduces predicted toxicity.

Looking Forward

- ***Mirror Lake Remediation & Restoration Project***
- Watershed Approach to Toxics Assessment and Restoration (WATAR)
  - *Collaboration between WAS & SIRS launched Fall 2012*
  - *Linking sources & sinks through forensics-grade monitoring*
  - *Old & new data being entered into EQUIS*
  - *Will identify opportunities for remediation and restoration*
  - *Toxics TMDLs where necessary*
- Begin backing off fish advisories

Mirror Lake Remediation/Restoration

- Mirror Lake Dover is impacted by PCBs, PAHs, and mercury
- Rather than dig it out, contaminants will be sequestered in place with SediMite
- Reduced recovery time expected
- Sand bar also to be converted to wetlands
- Construction Nov 2013 with pre- & post monitoring.



Legacy contaminants in exposed sediment contaminate the food chain through bioaccumulation in benthic organisms, flux into the water column, and uptake in the pelagic food web.

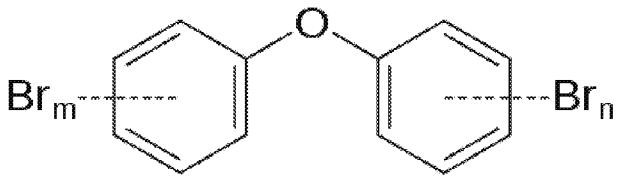
Activated carbon amended to surficial bioactive sediments reduces contaminant exposure to food chain through reduced bioaccumulation in benthic organisms and reduced flux into water column and uptake in the pelagic food web.

In the long term (>5 years), the carbon amended layer is covered with clean new sediment deposit and continues to serve as a barrier to the release of legacy contaminants to surficial sediments and water column.

Emerging Contaminants

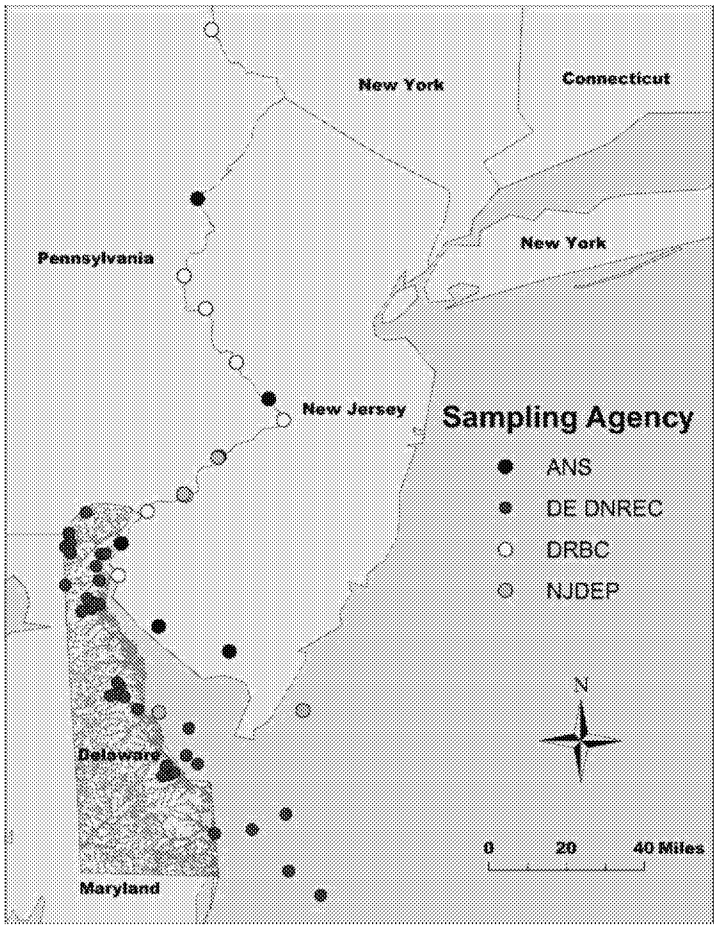
- ***Pharmaceuticals*** & personal care products (PPCP)
- ***Stain repellants/non-stick surfaces (PFCs)***
- ***Flame Retardants (PBDEs)***
- Sterols & hormones
- Surfactants (NP & NPEO)
- Plasticizers (bis-phenol-A and phthlates)
- Carbamate pesticides

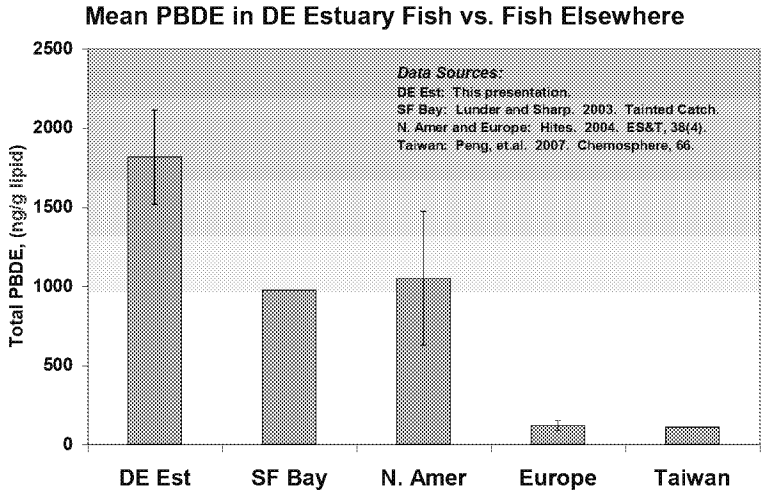
PBDEs

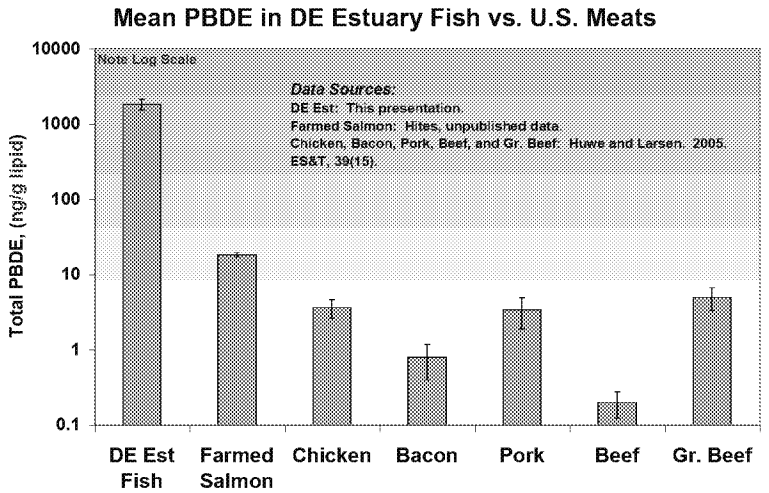


Organohalogens used in 1000s of consumer products as flame retardants. Similar to PCBs.

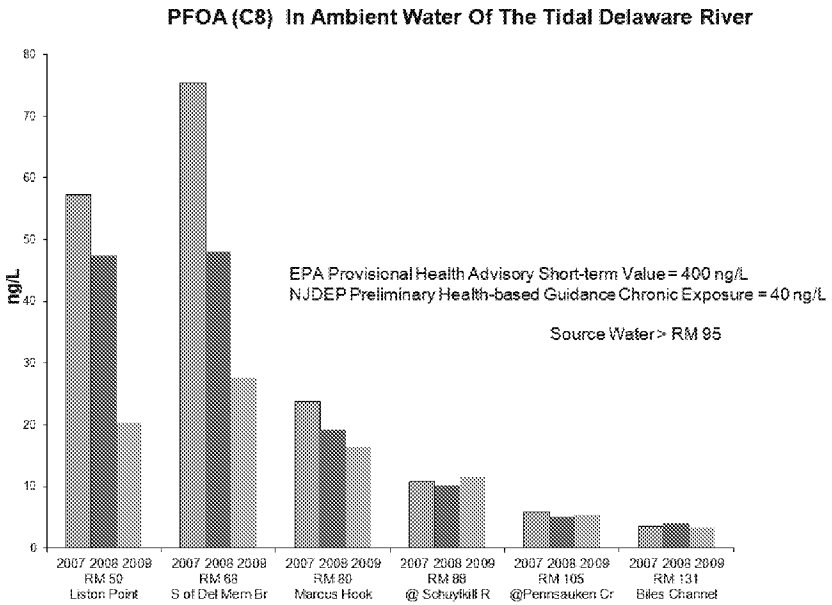
149 fish samples collected from Delaware River Basin , 55 locations, 18 species, 9/03-10/06

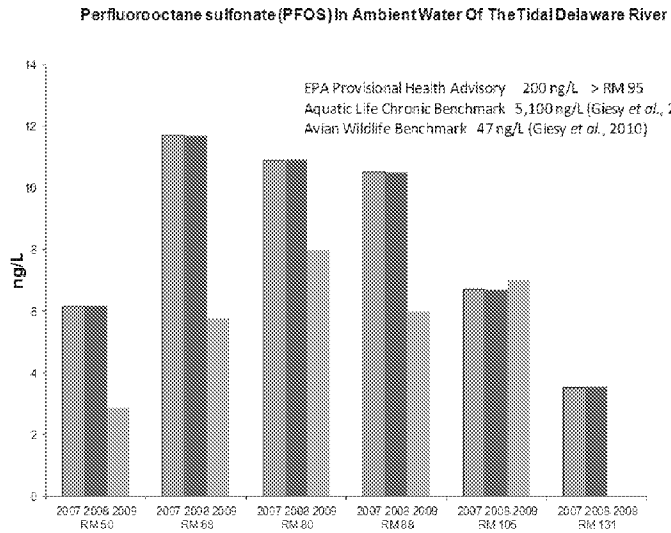






Fluorinated Compounds



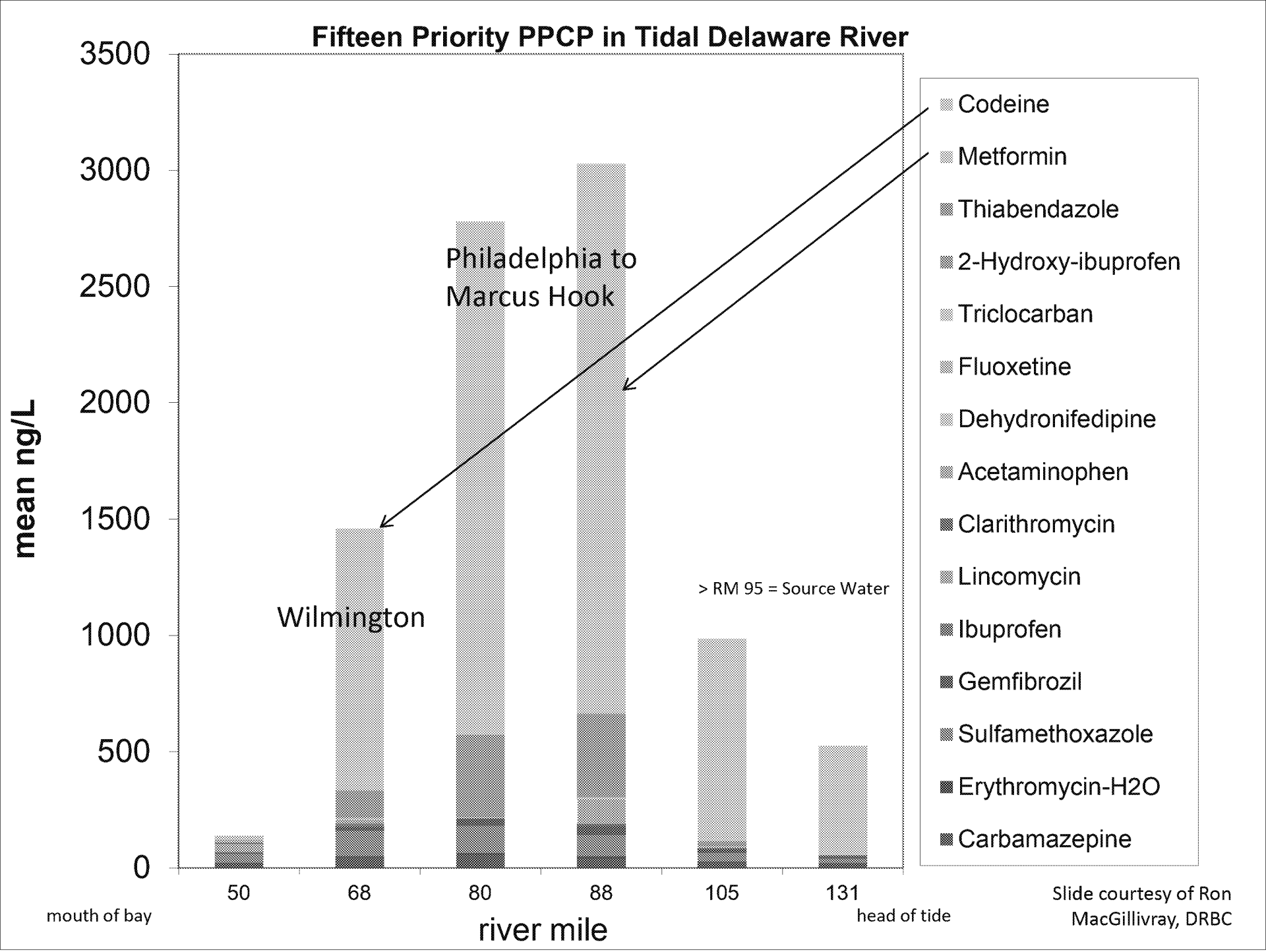


- DRBC monitored PFOA and PFOS in the tidal Delaware River between 2007 and 2009
- Peak for both compounds observed south of the Delaware Memorial Bridge
- Concentrations dropped between 2007 & 2009

Plots courtesy of Dr. Ron MacGillivray, DRBC

Pharmaceuticals

- DRBC also sampled the tidal Delaware River during this same time period for 15 PPCPs.
- Results similar to other urban waters with the exception of Metformin (used to treat type 2 diabetes) and Codeine (used in Extra Strength Tylenol)


Fifteen Priority PPCP in Tidal Delaware River
mean ng/L
3500
3000
2500
2000
1500
1000
500
0
Philadelphia to
Marcus Hook
Wilmington
> RM 95 = Source Water
Codeine
Metformin
Thiabendazole
2-Hydroxy-ibuprofen
Triclocarban
Fluoxetine
Dehydronifedipine
Acetaminophen
Clarithromycin
Lincomycin
Ibuprofen
Gemfibrozil
Sulfamethoxazole
Erythromycin-H2O
Carbamazepine
50
68
80
88
105
131
mouth of bay
river mile
head of tide
Slide courtesy of Ron
MacGillivray, DRBC

Summary

- Delaware's toxic legacy is slowly sunsetting
- Old threats coming under control or being dispersed; new threats emerging (or being revealed)
- Ample opportunity for collaboration and cooperation

Opportunities to Collaborate

- Role of SLR on waste sites & treatment infrastructure
- Framework for assessing & managing contaminated sediments.
- Biotic Ligand Model (BLM) for sediments.
- Variation of speciation & toxicity during rainfall-runoff events
- HRGC/HRMS capability
- Role of black carbon in partitioning
- Emerging contaminants
- Other

Selected References

- Ghosh U. and Greene R. 2012. In-situ Treatment of Mirror Lake Sediments to Reduce Uptake of Pollutants in the Food Chain. Proposal.
- Greene R., Di Toro D., et.al. 2013. Modelling water column partitioning of polychlorinated biphenyls to natural organic matter and black carbon. ES&T (in press).
- Greene R. 2010. An Evaluation of Toxic Contaminants in the Sediments of the Tidal Delaware River and Potential Impacts Resulting from Deepening the Main Navigation Channel in Reach C. DNREC, Dover, DE.
- Burton W. and Greene R. 2013. Natural Resource Damage Assessment Baseline Study, Delaware Estuary Polycyclic Aromatic Hydrocarbon (PAH) Pilot Study. Prepared for DNREC, New Castle, DE.
- Greene R. and Crecelius. Total and inorganic arsenic in Mid-Atlantic marine fish and shellfish and implications for fish advisories. Integ Environ Assess Manag 2(4): 344-354.
- Greene R. 2008. Amended Total Maximum Daily Load (TMDL) for Zinc in the Red Clay Creek, Technical Background and Basis Document. DNREC, Dover, DE.
- Greene R. and Stangl M. 2012. Feasibility of Stocking Red Clay Creek with Trout. Report. DNREC, Dover, DE.
- Greene R. 2006. Trends in Contaminants of Concern in Delaware Estuary Fish. Presentation. DNREC, Dover, DE.
- Greene R. 2008. Dioxins and Furans in Fish from the Delaware River. Presentation DNREC, Dover, DE
- Greene R. 2010. Arsenic in the Delaware Inland Bays. Presentation. DNREC, Dover, DE.
- Greene R. 2010. Polybrominated Diphenyl Ethers (PBDEs) in Fish from the Delaware River Drainage Basin. Presentation. DNREC, Dover, DE.
- Greene R. 2007. Mercury in Delaware Surface Water. Presentation. DNREC, Dover, DE.
- MacGillivray R. et.al. 2011. Monitoring the tidal Delaware River for ambient toxicity. Integ Environ Assess Manag 7(3): 466-477.
- MacGillivray R. 2012. Contaminants of Emerging Concern in the Tidal Delaware River, Pilot Monitoring Survey. Report. Delaware River Basin Commission, West Trenton, NJ.
- Mason, R. 2011. The Cycling and Fate of Mercury and Methylmercury in the Sub-Tidal Reaches of the Delaware Estuary. Proposal.
- Velinsky D, Sommerfield C, and Charles D. 2010. Vertical Profiles of Radioisotopes, Contaminants, Nutrients and Diatoms in Sediment Cores from the Tidal Christina River Basin: A Historical Analysis. Reported prepared by ANSP and UD for DNREC, Dover, DE.
- Velinsky D, Charles D, Sommerfield C, Greene R, and Fikslin T. 2011. Tidal Marshes in the Delaware Estuary: Historical Reconstruction of Chemical Loadings. Presentation.

Thank You

Rick Greene

richard.greene@state.de.us

(302) 739-9939

www.dnrec.delaware.gov